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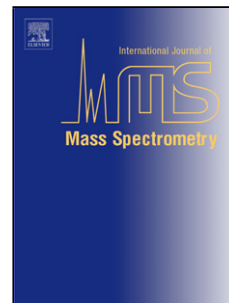
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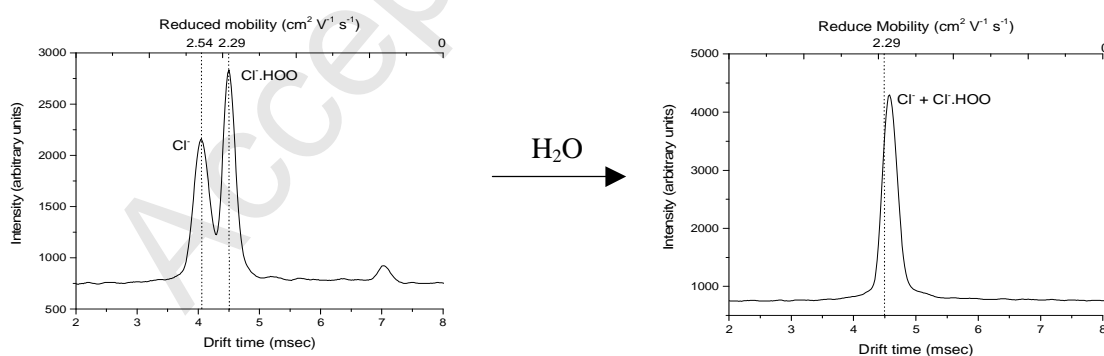
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Ion mobility studies on the negative ion-molecule chemistry of pentachloroethane

HIGHLIGHTS

- Investigation of the negative ion-molecule chemistry of pentachloroethane, PCE, in both nitrogen and air for both Ion Mobility Spectrometry (IMS) and Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) systems.
- Based upon the moisture content of the system, product ions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system.
- Extra care that must be taken in interpreting even apparently simple chemical systems in an IMS instrument.

GRAPHICAL ABSTRACT



ION MOBILITY STUDIES ON THE NEGATIVE ION-MOLECULE CHEMISTRY OF PENTACHLOROETHANE

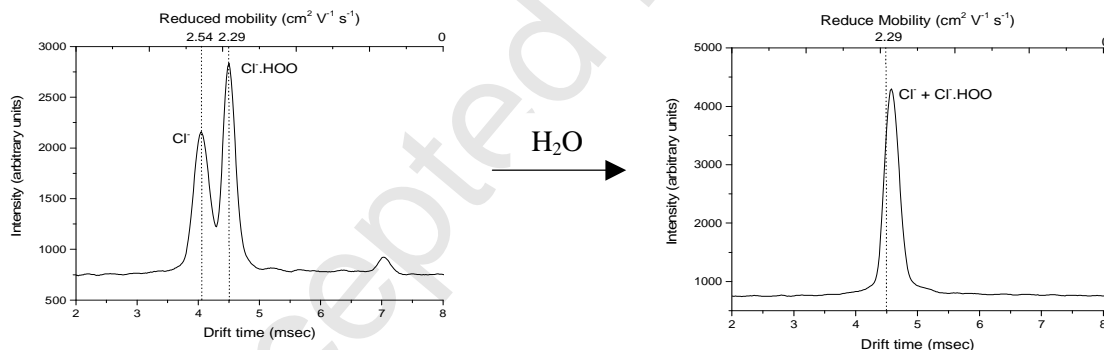
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Key words: Ion Mobility Spectrometry; IMS-MS; Pentachloroethane; Chlorinated Ethane; Ion-Molecule Chemistry

GRAPHICAL ABSTRACT



Abstract

In this study we present an investigation of the negative ion-molecule chemistry of pentachloroethane (PCE) in air based Ion Mobility Spectrometry and Ion Mobility Spectrometry-Mass Spectrometry systems. The observed product ions are Cl^- , produced by dissociative electron attachment, and $\text{Cl}^-\cdot\text{HOO}$ resulting from a reaction with O_2^- . Based upon the moisture content of the system, these ions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system. The nature of the $\text{Cl}^-\cdot\text{HOO}$ product ion was investigated by using isoflurane (ISOF) as a probe to monitor the changing ratios of Cl^- and $\text{Cl}^-\cdot\text{HOO}$ as the PCE concentration decreased. This confirmed the origins of the two product anions. Electronic structure calculations are provided. These have aided the understanding of the reaction processes observed.

1. Introduction

The ability to quickly and accurately identify hazardous compounds, and particularly within a complex chemical environment, is vital to homeland security. Ion Mobility Spectrometry (IMS) has found worldwide deployment in security areas such as airports. However, it has limitations in terms of selectivity, and false positives do occur. To limit these, the ion chemistry in the reaction of the region of the IMS can be manipulated. This is achieved by doping the carrier gas. Chlorine containing compounds are used in ion mobility spectrometers operating in negative ion mode to enhance specificity and sensitivity.¹⁻¹² Unfortunately the most suitable, in terms of its facile dissociative electron attachment (DEA) with thermal electrons and its volatility, is carbon tetrachloride, CCl_4 , which is now banned by the Montreal Protocol.¹³ Hexachloroethane, HCE, is commonly used in laboratory investigations, and has been described in a recent paper on the ion-molecule chemistry of the anaesthetics isoflurane (ISOF, $\text{CF}_3\text{CHClOCHF}_2$) and enflurane (ENF, $\text{CHF}_2\text{OCF}_2\text{CHFCl}$).¹⁴ However, its vapour pressure at low temperatures makes it unsuitable for use in practical systems for use in the field. The volatility of pentachloroethane, PCE ($\text{CCl}_3\text{CHCl}_2$), makes it more suitable for use in such practical devices as the Smiths Detection Lightweight Chemical Detector used in this study.¹⁵

The investigation presented in this paper continues our work on the negative ion-molecule chemistry of chlorinated compounds in IMS systems.¹⁴ Two systems have been used for this work, a Smiths Detection IMS - henceforth referred to as the Smiths system,¹⁵ and a home-made IMS/MS located in the Molecular Physics Group at the University of Birmingham - referred to as the Birmingham system. An additional motivation for this study comes from preliminary experiments with PCE, which in the Birmingham IMS/MS system showed only one ion mobility peak, whilst the Smiths IMS system showed a doublet peak structure. The results of the present study, which used ISOF as a probe compound, allowed these apparently conflicting observations to be rationalised.

The experimental work presented in this paper is supported by electronic structure calculations at the B3LYP level, which provide useful energetic calculations for the DEA processes and various chemical reactions.

2. Experimental Details

2.1. Ion Mobility Spectrometry (IMS) and Ion Mobility Spectrometry-Mass Spectrometry (IMS/MS)

The Birmingham IMS/MS system used in this study has been described elsewhere,¹⁶⁻²⁰ and hence only a brief description is provided here. This instrument consists of two glass drift tube regions each of 10 cm in length. The first, the reaction region containing a cylindrical radioactive ion source (nominal 10 mCi ⁶³Ni foil), is physically separated from the second region, the drift region, by a Bradbury-Nielson (B-N) gate. A forward flow of the buffer gas flows through the radioactive source and into the glass jacket towards the B-N grid. A contraflow of the same buffer gas is introduced through apertures near to a Faraday plate (FP). The analyte of interest is introduced in the forward flow with the help of syringes. Forward and contraflows are set at 0.4 L min⁻¹ and 0.8 L min⁻¹ (at slightly above the ambient atmospheric pressure and room temperature), respectively, and controlled by mass flow controllers (Alicat Scientific, Arizona, USA, $\pm 1\%$ accuracy). The two flows are vented out of the drift tube through holes in the B-N ring. The drift tube's pressure is measured with a strain gauge absolute pressure sensor (Edwards, West Sussex, UK, model ASG 2000). A thermocouple is used to monitor the temperature of the buffer gas near to the exhaust region and the temperature of the drift tube is electronically controlled at a constant temperature of $30 \pm 1^\circ\text{C}$. An electric field along the axis of the drift tube is set at 200 V cm⁻¹.

The FP is protected by a screen grid to shield it from the electric field produced by the oncoming ion swarm. At the centre of the FP there is a 0.07 mm pinhole, separating the IMS from the lower pressure quadrupole mass spectrometer region. The product ions are separated according to their m/z values using quadrupole mass filter and detected using a secondary electron multiplier. For this identification of the m/z values the B-N grid in the drift tube is kept open in order to maximise ion signal intensity.

To obtain ion mobility spectra, the B-N gate is used to pulse reactant and product ions generated in the reaction region into the drift region tube at a frequency of 25 Hz and a pulse width of 600 μs (600 μs was necessary, because at shorter pulse widths the ion signals associated with isoflurane and enflurane were significantly weaker, presumably owing to the transit times of the product ions through the B-N grid). Mobility spectra were acquired by means of purposely written software using Labview.²⁰ Total ion mobility spectra were acquired using the FP. Tuned ion mobility spectra were obtained by sampling ions through the FP and then allowing a specific m/z through the mass filter. The tuned ion mobility spectra were used to verify contributions of product ions to the individual peaks in the total ion mobility spectra.²⁰

The Smiths system used is a modified Lightweight Chemical Detector (LCD).^{15,21} Two IMS cells, one for positive ions and one for negative ions, are housed in the same

instrument. The data presented in this paper were acquired in the negative mode cell. Each cell consists of two regions: reaction and drift regions. The reaction region, containing a dual-point corona discharge ionization source,²² is open to ambient air via a pinhole through which air is pulled into the system for sampling. Connected to the reaction region are On-demand Vapour Generators (OVGs) for injecting PCE and isoflurane in the system.²³ The ions generated in the reaction region migrate under the influence of an electric field towards a B-N gate. Once transferred through the B-N gate in the drift region, the ions drift towards a FP for detection. The electric field, generated by applying a voltage gradient across the electrodes placed along the whole drift tube length (reaction and drift regions), was set to be about 200 V cm⁻¹. The drift gas has a flow of 150 mL min⁻¹ and consists of air at atmospheric pressure. It is generated by a fan which recirculates air through the IMS cells and a molecular sieve. The molecular sieve traps water in order to keep a low level of moisture in the system. In order to increase the moisture level in the IMS cell, a fraction of the drift gas was pumped from the body of molecular sieve, circulated in the headspace above a saturated solution of lithium chloride (headspace air with relative humidity of 11.30%), and mixed back into the drift air flow close to the FP.

2.2 Procedures and chemicals

Isoflurane (with stated purity of 99%) was purchased from Sigma Aldrich (Dorset, UK). Pentachloroethane (96% pure) was purchased from Alfa Aesar (Lancashire, UK). All the samples were used without further purification. At room temperature they are both liquids.

In the Birmingham system, typically 50 µL were spotted onto cotton and placed inside a glass syringe (Weber Scientific, New Jersey, USA) which was inserted through a septum into the forward flow at a constant rate using a syringe driver (Cole Palmer 74900 series, Illinois, USA). In the Smiths system, OVGs were used as the sampling method.

Zero air grade and pure nitrogen (oxygen free and 99.998% purity) carrier gases used for this experiment were purchased from BOC Gases (Manchester, UK). Prior to entering the reaction region all carrier gases were passed through moisture and hydrocarbon traps (Supelco 23991 and Agilent BHT-4 respectively).

2.3. Density Functional Theory (DFT) Calculations

These were conducted using Gaussian09W and GaussView05 for Windows.²⁴ Unless otherwise stated all calculations used the B3LYP functional and the 6-31+G(d,p) basis set, a combination which has been found to be satisfactory.¹⁴ Stable species were characterised by

the absence of an imaginary frequency. Vertical Attachment Energies (VAEs) were determined by doing a frequency job after placing a negative charge on the ground state geometry of the neutral.

3. Results and Discussion

3.1 Pentachloroethane

3.1.1 Electron attachment

DEA in nitrogen to give both Cl^- and Cl_2^- is thermodynamically favourable (Table 1) although only the former is observed.

Table 1. Calculated ΔH s and ΔG s for the DEA of PCE leading to Cl^- and Cl_2^- . DFT calculations were performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Ionic products	$\Delta H_{298} \text{ kJ mol}^{-1}$	$\Delta G_{298} \text{ kJ mol}^{-1}$
PCE + e	Cl^-	-119	-161
	Cl_2^-	-190	-244

The calculated VAE is negative (-7.0 kJ mol^{-1}) as expected from the observed resonance with electrons at 0 eV. No Cl_2^- was observed, although it is reported to occur at 0 eV by Matias *et al* in a study involving DEA at low pressures.²⁵

3.1.2 Reactions in air

In the Birmingham system only a single IMS peak was observed. Tuned m/z experiments showed it to be a mixture of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n=0,1$) and m/z 68. Figure 1 shows the Reactant Ion Peak (RIP) for (a) air (b) for PCE (obtained in the system sufficiently doped with PCE for the air RIP to be fully depleted).

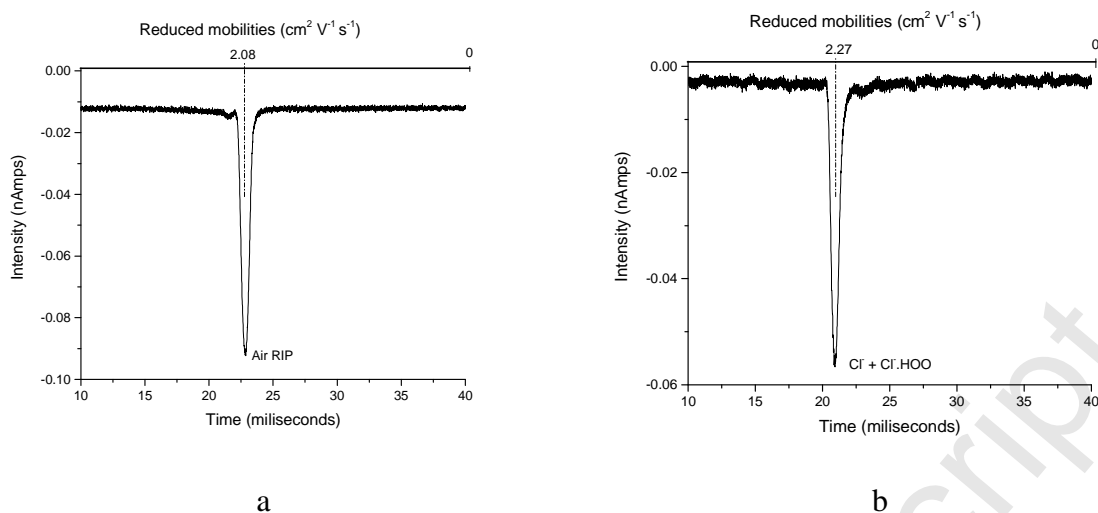


Figure 1. IMS spectra showing the RIP for (a) an air system and (b) for a heavily doped PCE system. In all figures only the core ions are given in the annotations, water clusters have been omitted.

As the concentration of PCE reduced, but with the air RIP still completely depleted, a peak on the low mobility side of the PCE RIP appeared (figure 2). Tuned ion mobility showed that this results from an anion at m/z 68. This is ascribed to be $\text{Cl}^-\text{.HOO}$ (see later).

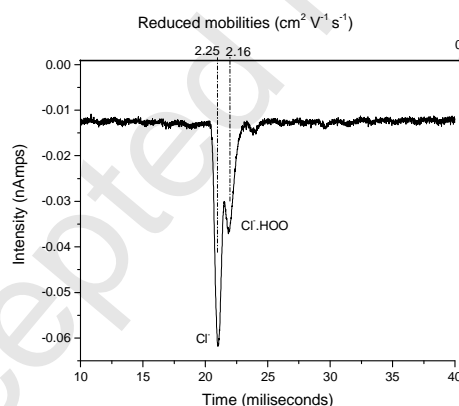


Figure 2. IMS spectrum in an air system doped with PCE at a lower concentration of PCE than in figure 1 (b), but still sufficiently high to completely deplete the air RIP.

In the Smiths system (see Figures 3a and 3b), under very dry conditions (it is not possible to be quantitative at such low water concentrations in such a small IMS device) either a singlet or a doublet or various intermediate mobility peaks could be observed dependent upon the PCE and water concentrations. In Figures 3a and 3b the more mobile peaks are ascribed to Cl^- and the less mobile peaks to $\text{Cl}^-\text{.HOO}$. Figure 3a shows that as the humidity increases the Cl^- peak decreases in mobility due to hydration subsequently merging

193 with the $\text{Cl}^-\cdot\text{HOO}$. As will be seen later, Cl^- readily complexes with one H_2O molecule,
 194 whereas $\text{Cl}^-\cdot\text{HOO}$ does not. Figure 3b shows that as the PCE concentration increases the ratio
 195 $\text{Cl}^-\cdot\text{HOO}$ to Cl^- decreases.

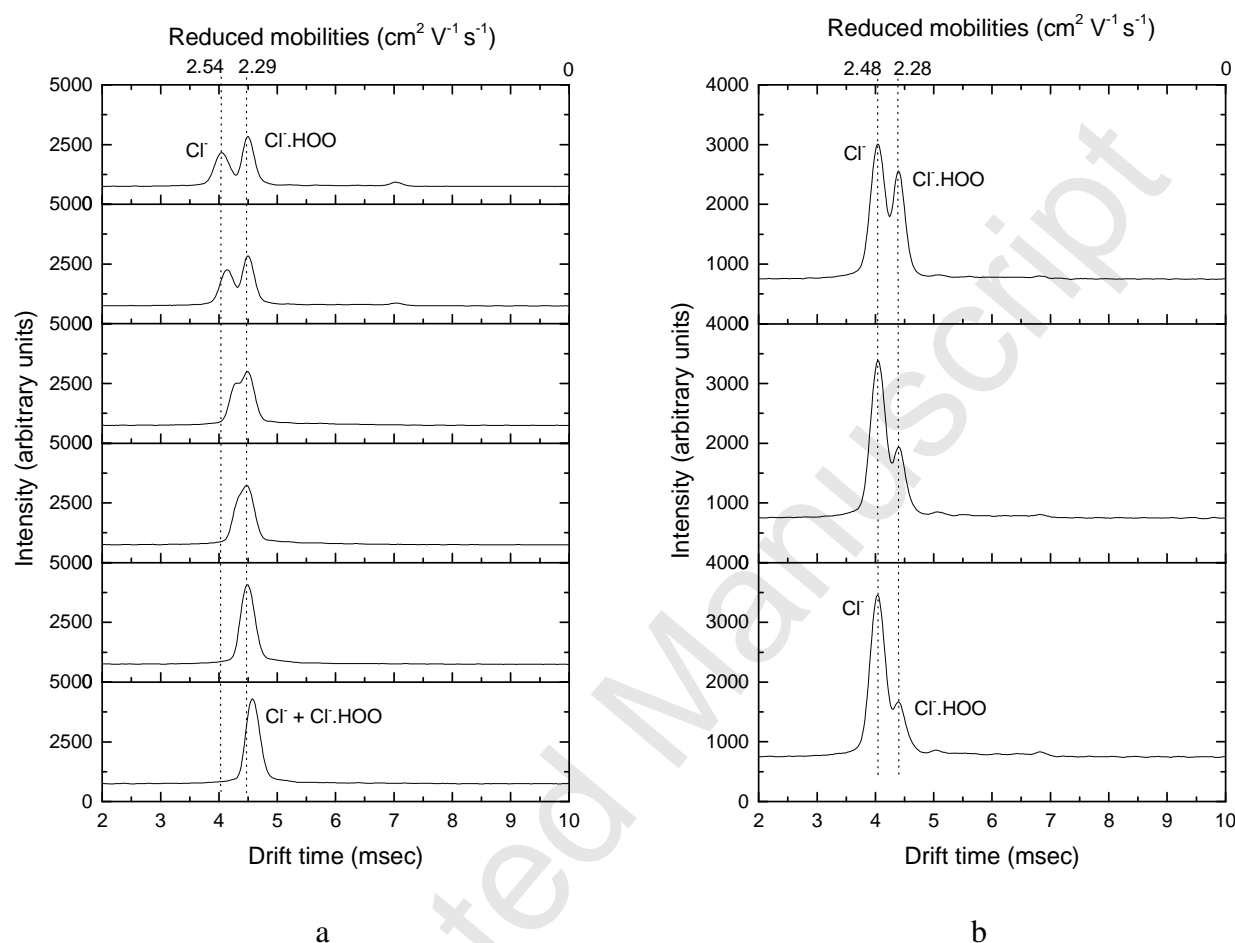


Figure 3. (a) IMS spectra of PCE showing the effect of the internal moisture and how, as the humidity increases, the Cl^- peak decreases in mobility due to hydration subsequently merging with the $\text{Cl}^-\cdot\text{HOO}$ peak. The level of moisture gradually increases from the top to the bottom plot. (b) IMS spectra of PCE acquired at different PCE concentrations showing the effect of the PCE concentration on the relative intensities of Cl^- and $\text{Cl}^-\cdot\text{HOO}$. The PCE concentration gradually increases from the top to the bottom plot.

A detailed inspection of the results showed that, dependent upon the PCE and water concentrations, either a singlet or a doublet or various intermediate mobility peaks could be observed both in the Smiths and Birmingham systems.

The ion with m/z 68 is assigned as $\text{Cl}^-\cdot\text{HOO}$ as DFT calculations showed that it is essentially Cl^- hydrogen bonded to HOO (figure 4).

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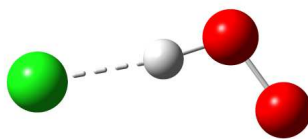


Figure 4. Structure of $\text{Cl}^\cdot\text{.HOO}$ obtained from DFT calculations.

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205 The same result is obtained starting from Cl^\cdot associating with OOH as from HCl
 206 associating with O_2^\cdot . As electron attachment to PCE in the IMS system gives only Cl^\cdot , it can
 207 be safely assumed that the formation of $\text{Cl}^\cdot\text{.HOO}$ arises from the reaction of PCE with O_2^\cdot .
 208 The overall energetics for this reaction are $\Delta H_{298} -180 \text{ kJ mol}^{-1}$ and $\Delta G_{298} -196 \text{ kJ mol}^{-1}$,
 209 assuming that the neutral product is CCl_2CCl_2 . This is supported by the observation that as
 210 the concentration of PCE increased so did the proportion of Cl^\cdot as would be expected if O_2
 211 and PCE are in competition for the electrons. The initial (albeit transient) product of the
 212 reaction of O_2^\cdot with PCE is a complex with the oxygen close to the hydrogen of the PCE, as
 213 shown in Figure 5, and Table 2 for the energetics. An alternative conformation with the
 214 oxygen orientated away from the CCl_3 group is slightly less stable.

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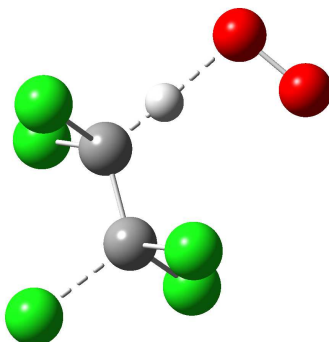


Figure 5. Structure of PCE.O_2^\cdot complex obtained from DFT calculations.

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221 Table 2. Energetics for the formation of various species relative to $\text{PCE} + \text{O}_2^\cdot$. DFT
 222 calculations were performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reaction	Species	$\Delta H_{298} \text{ kJ mol}^{-1}$	$\Delta G_{298} \text{ kJ mol}^{-1}$
1	Complex PCE.O ₂ ⁻ (Fig 4)	-104	-73
2	C ₂ Cl ₅ ⁻ + HOO	-82	-107
3	C ₂ Cl ₄ + Cl ⁻ + HOO	-70	-113
4	C ₂ Cl ₄ + Cl ⁻ .HOO	-180	-196
5	CHCl ₂ CCl ₂ + Cl ⁻ + O ₂	-59	-102
6	Barrier for rotation around the C-C bond of PCE	+38	+43
7	Barrier for rotation around the C-C bond of PCE.O ₂ ⁻	+33	+22

Of primary interest is the formation of Cl⁻.HOO. Reactions 3 and 5 may contribute to the production of Cl⁻ but are probably of little importance compared to the DEA with free electrons. It is not proposed that reactions 2 and 3 occur (except as precursors to reaction 4) but are included to illustrate that sufficient energy is available in the transient PCE.O₂⁻ complex to allow complex conformational changes to occur. This is necessary as formation of Cl⁻.HOO from the complex (reaction 4) requires a concerted lengthening on the C-H bond and a rotation of the C-Cl bonds around the C-C bond. Despite many attempts no transition state has yet been found, and this difficulty is attributed to the proposed concerted nature of the transition state.

3.1.3 Reactions of H₂O with Cl⁻ and Cl⁻.HOO

It can be seen from Table 3 that Cl⁻ will readily complex with one water, but that Cl⁻.HOO will not as the HOO is effectively solvating Cl⁻, i.e. taking the place of H₂O in the Cl⁻.H₂O complex. The strength of the Cl⁻.HOO complex can be seen in the last row of Table 3. Thus in a 'dry' system the doublet of Cl⁻ and Cl⁻.HOO is observed and as the water concentration increases the Cl⁻ complexes with water thus decreasing its mobility and eventually merging with the Cl⁻.HOO to give a singlet (see Figure 1b).

Table 3. Calculated ΔH s and ΔG s for the reactions of Cl⁻.(H₂O)_n (n = 0, 1 and 2) with H₂O, Cl⁻ with HOO, and Cl⁻.HOO.(H₂O)_n (n = 0 and 1) with H₂O. DFT calculations performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Products	$\Delta H_{298} \text{ kJ mol}^{-1}$	$\Delta G_{298} \text{ kJ mol}^{-1}$
$\text{Cl}^- + \text{H}_2\text{O}$	$\text{Cl}^-\cdot\text{H}_2\text{O}$	-60	-37
$\text{Cl}^-\cdot\text{H}_2\text{O} + \text{H}_2\text{O}$	$\text{Cl}^-\cdot 2\text{H}_2\text{O}$	-54	-18
$\text{Cl}^-\cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}$	$\text{Cl}^-\cdot 3\text{H}_2\text{O}$	-47	-10
$\text{Cl}^-\cdot\text{HOO} + \text{H}_2\text{O}$	$\text{Cl}^-\cdot\text{HOO}\cdot\text{H}_2\text{O}$	-52	-16
$\text{Cl}^-\cdot\text{HOO}\cdot\text{H}_2\text{O} + \text{H}_2\text{O}$	$\text{Cl}^-\cdot\text{HOO}\cdot 2\text{H}_2\text{O}$	-44	-7
$\text{Cl}^- + \text{HOO}$	$\text{Cl}^-\cdot\text{HOO}$	-111	-83

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246 **3.2 Reaction of ISOF in a PCE doped system**

247 As a way to fully understand the occurring chemistry, the properties of the $\text{Cl}^-\cdot\text{HOO}$ ion were
 248 investigated by using ISOF as a probe in both instruments. For such a purpose sufficient PCE
 249 was introduced to replace the air RIP (figure 1a) with a PCE RIP of Cl^- and $\text{Cl}^-\cdot\text{HOO}$ (figure
 250 1b). In the Birmingham system, addition of ISOF (shown in Figure 6a) results in the
 251 formation of two product ions m/z analysed as $\text{ISOF}\cdot\text{Cl}^-$ and $\text{ISOF}\cdot\text{Cl}^-\cdot\text{HOO}$ the latter being
 252 the less mobile peak. The IMS spectrum in Figure 6b (when compared with that shown in
 253 figure 6a) demonstrates the variability in relative proportions of product ions. For figure 6b
 254 the PCE concentration had been allowed to decay as can be seen by the appearance of the air
 255 RIP at reduced mobility $K_0 = 2.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In Section 3.1.2 it was suggested that as the
 256 PCE concentration decreased the ratio of $\text{Cl}^-\cdot\text{HOO}/\text{Cl}^-$ would increase, and this is well
 257 demonstrated by the changing ratios of $\text{ISOF}\cdot\text{Cl}^-$ and $\text{ISOF}\cdot\text{Cl}^-\cdot\text{HOO}$ in Figures 6a and 6b.

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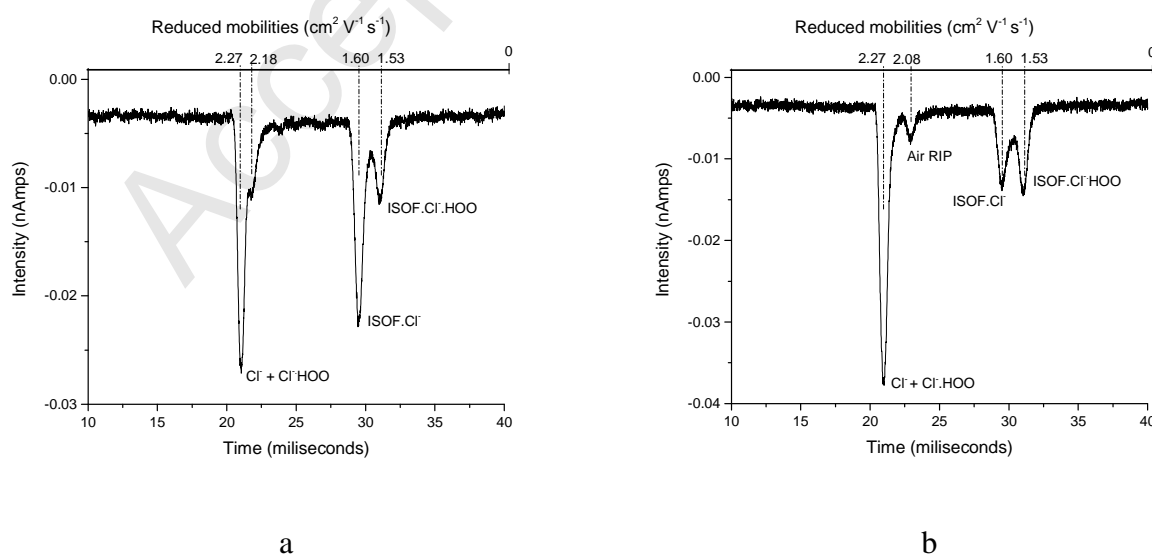


Figure 6. (a) IMS spectrum for an air system doped with PCE with ISOF added. (b) IMS

spectrum for an air system doped with PCE (in lower concentration when compared with 6a) following addition of ISOF. The small peak at $K_0 = 2.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is the remnant of the air RIP.

For the Smiths system results of similar experiments are shown in figure 7 under wet and dry conditions.

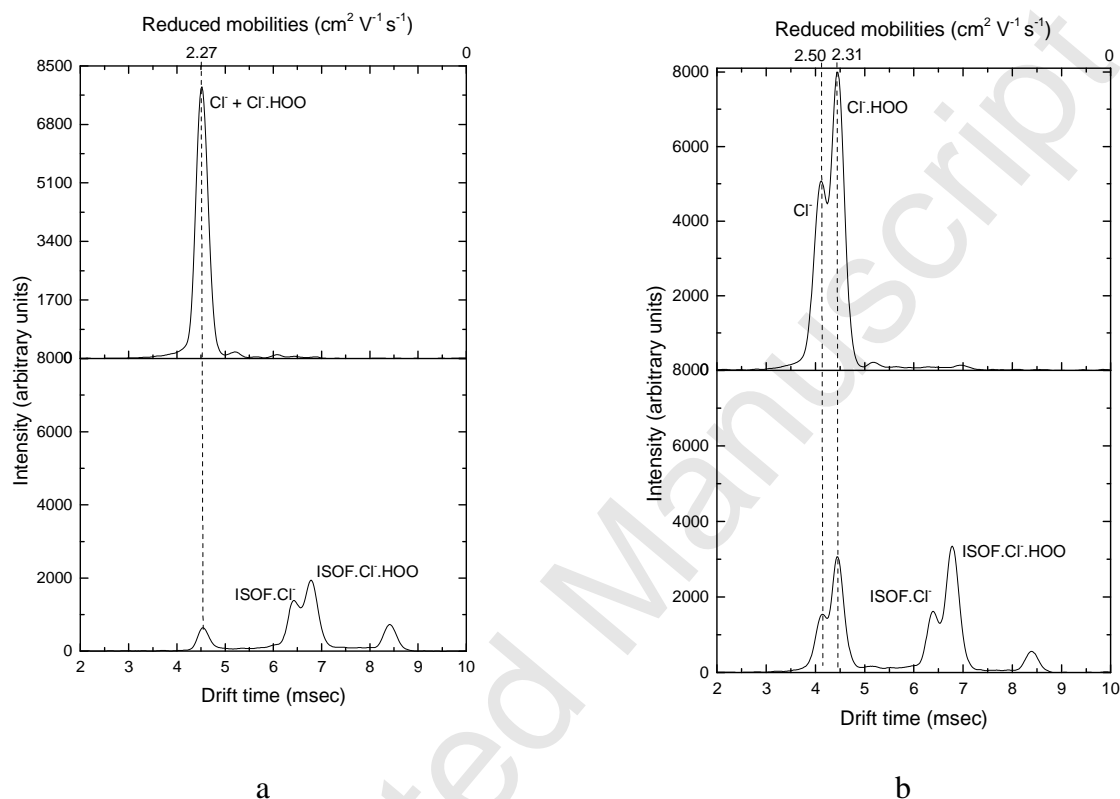


Figure 7. Smiths IMS spectra of PCE (top line plots) and ISOF (bottom line plots) acquired in a PCE doped system in a) “wet” conditions; b) “dry” conditions.

DFT calculations provided stable structures for the $\text{ISOF.Cl}^-\text{.HOO}$ and ISOF.Cl^- product ions, as shown in Figure 8.

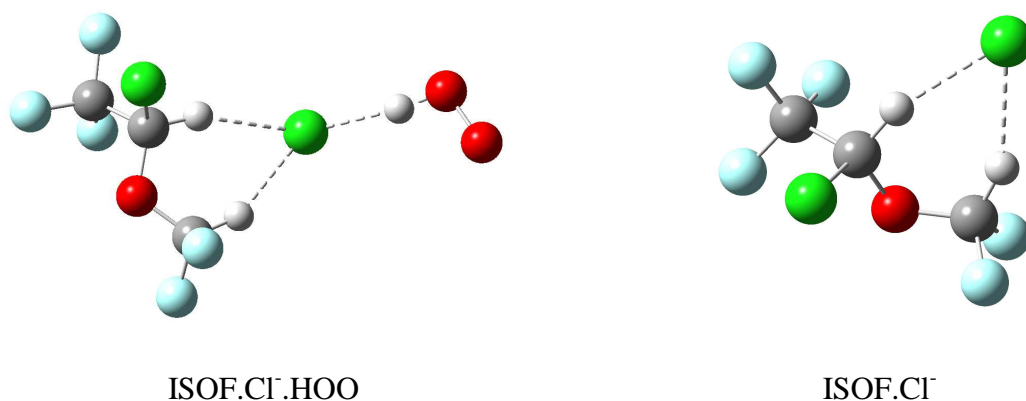


Figure 8. Structure of ISOF monomer product ions $\text{ISOF.Cl}^-\text{.HOO}$ and ISOF.Cl^- obtained

from DFT calculations.

The energetics for the reactions of ISOF with Cl^- and $\text{Cl}^-\cdot\text{HOO}$ are summarised in Table 4.

Table 4. ΔH s and ΔG s for the reaction of ISOF with various anions. DFT calculations performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Ionic Products	$\Delta\text{H}_{298} \text{ kJ mol}^{-1}$	$\Delta\text{G}_{298} \text{ kJ mol}^{-1}$
$\text{ISOF} + \text{Cl}^-\cdot\text{HOO}$	$\text{ISOF}\cdot\text{Cl}^-\cdot\text{HOO}$	-76	-50
$\text{ISOF}\cdot\text{Cl}^-\cdot\text{HOO} + \text{ISOF}$	$\text{ISOF}_2\cdot\text{Cl}^-\cdot\text{HOO}$	-58	-2
$\text{ISOF} + \text{Cl}^-$	$\text{ISOF}\cdot\text{Cl}^-$	-108	-79
$\text{ISOF}\cdot\text{Cl}^- + \text{ISOF}$	$\text{ISOF}_2\cdot\text{Cl}^-$	-74	-40

Calculations showed that the dimer complex of ISOF and $\text{Cl}^-\cdot\text{HOO}$ is thermo neutral and even if formed it will be unstable in the drift region and hence is unlikely to be observed in accord with experiment.

4. Conclusions

After introduction of PCE into an air based IMS system, two product ions were observed, Cl^- by DEA and $\text{Cl}^-\cdot\text{HOO}$ by reaction with O_2^- . These anions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system. In the wet system Cl^- clusters with water thus reducing its mobility whereas $\text{Cl}^-\cdot\text{HOO}$ does not. Because DEA and reaction with O_2^- are in competition the ratio of the two product ions is dependent upon PCE concentration. An additional factor leading to this dependence is that PCE and O_2 are competing for electrons, the PCE leading to Cl^- through DEA and the O_2 leading to O_2^- . $\text{Cl}^-\cdot\text{HOO}$ complexes with ISOF as does Cl^- . This is nicely demonstrated by two ISOF product peaks being observed even in a wet system when only a singlet PCE based RIP is observed.

The results presented here illustrate the care that must be taken in interpreting even apparently simple chemical systems in an IMS instrument. Electronic structure calculations have provided valuable insight into the processes observed.

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